<Solid State Chemistry> Advanced Inorganic Synthesis

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- Advanced Inorganic Synthesis -

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Scope of Research

Transition-metal oxides show lots of interesting and useful properties. They include ferroelectrics, ferromagnets, conductors, batteries, and so on. These materials are widely used in current electronic devices. The wide variety of their crystal structures gives rise to various electronic structures, which lead to interesting and useful physical and chemical properties. We are focusing on the fundamental physics and chemistry of these "functional oxides" and seeking new materials with new functions. We are conducting systematic studies of material synthesis based on phase equilibrium information. Precise crystal structures are analyzed by x-ray and neutron diffraction. Electronic and magnetic structures are discussed based on the results of electronic structure calculations and physical property measurements.

Research Activities (Year 2003)

Presentations

Magnetic properties of La,Co substituted *M*-type Sr-ferrite synthesized by the polymerized complex method, Kikuchi M, Nakamura T, Nakamura M, Miki M, Nakanishi M, Fujii T, Takada J, Ikeda Y, The 91st Annual Meeting of the Society of Powder and Powder Metallurgy, Tokyo, 22 May.

Low-temperature synthesis of *M*-type hexagonal ferrite by the polymerized complex method, Kikuchi M, Nakamura T, Nakamura M, Miki M, Nakanishi M, Fujii T, Takada J, Ikeda Y, The 91st Annual Meeting of the Society of Powder and Powder Metallurgy, Tokyo, 22 May.

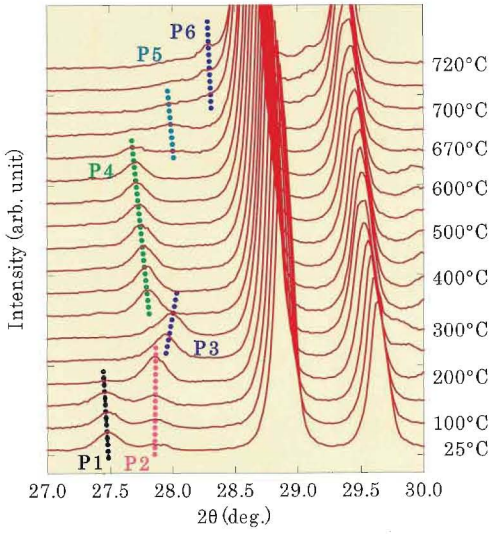
Magnetic properties of La,Co substituted *M*-type Sr-ferrite synthesized by the Citrate-method, Kikuchi M, Tanaka K, Nakamura T, Nakamura M, Miki M, Nakanishi M, Fujii T, Takada J, Ikeda Y, The 92nd Annual Meeting of the Society of Powder and Powder Metallurgy, Osaka, 6 November.

Magnetic properties of Co,Sn substituted *M*-type Ba-ferrite synthesized by the Citrate-method, Kikuchi M, Ashioka J, Nakamura T, Nakamura M, Miki M, Nakanishi M, Fujii T, Takada J, Ikeda Y, The 92nd Annual Meeting of the Society of Powder and Powder Metallurgy, Osaka, 6 November.

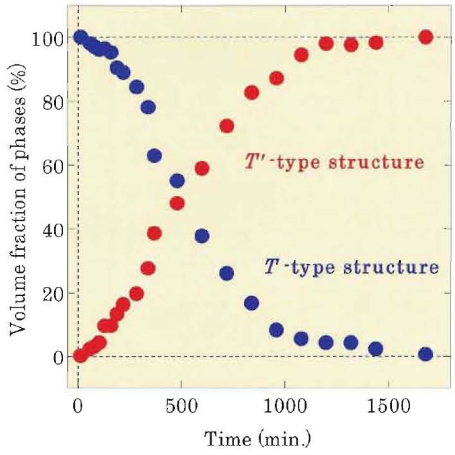
Phase diagrammatic studies on high-*Tc* superconducting oxides

One of the most novel classes of transition-metal oxides is the high-*Tc* superconductors. $Bi_2Sr_2CuO_{6+\delta}$ has been expected to provide crucial information about the superconducting mechanism due to its simple crystal structure and chemical composition. However, our careful phase diagrammatic studies on this compound revealed that there are at least six phases with different oxygen contents. The oxygen contents are controlled by changing the annealing temperature. The variation in oxygen contents causes changes in carrier concentration of the materials, and thus leads to the variation in superconducting transition temperature, ranging from 0 (an insulator) to 26 K.

$Pr_{2-x}La_xCuO_4$ is a related compound to high-*Tc* superconducting oxides. When samples with $1.35<x<1.5$ are quenched after annealing at 1000°C, they show a *T*-type crystal structure, which is the same as that of hole-doped $La_{2-x}Sr_xCuO_4$. Interestingly, $Pr_{2-x}La_xCuO_4$ gradually changes its structure from *T*-type to *T'*-type, which is the typical structure for electron-doped $Pr_{2-x}Ce_xCuO_4$, even at room temperature. Since ion diffusion in solids is extremely low at room temperature, the observed behavior is quite peculiar. It might be related to microscopic electronic phase separation, which is one of the recent key issues concerning strongly correlated electron systems.



High-temperature x-ray diffraction patterns of $Bi_2Sr_2CuO_{6+\delta}$. The oxygen content decreases with increasing temperature. P1 — P6 denote superstructure diffraction peaks of phases with different oxygen contents.



Phase transformation of $Pr_{2-x}La_xCuO_4$ from a *T*-type to *T'*-type structure.

Novel functional oxides

In transition metal oxides, the cation-*d*-orbital and anion-*p*-orbital are strongly hybridized. Competitive and/or cooperative energies of Coulomb interaction, bandwidth, and exchange interaction also play an important role in giving rise to a wide variety of physical and chemical properties. Such exotic properties could be useful for the functions of electronic devices. There are many examples of such functional oxides: Li-ion batteries are Li-containing Co- or Ni-oxides, and FeRAMs (ferroelectric random access memories) used in IC cards consist of $Pb(Zr,Ti)O_3$ or Bi-containing Ta oxides. Recent significant developments in x-ray and neutron diffraction techniques enable us to determine the detailed crystal structures of such oxides. The information about the structures provides a basis for electronic structure calculations. Therefore, we discuss the relationships between the fundamental physics and useful functions of the functional oxides.

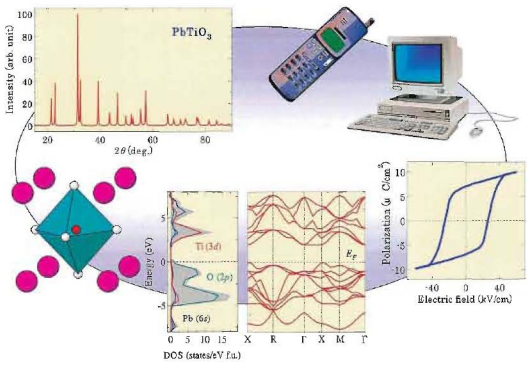


Illustration of our research processes.